

**GENCORP**  
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06 August 1997

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Dear Mr. Berrey, Mr. MacDonald, and Mr. Austin:

Please find enclosed the report entitled: *"Report on the Laboratory Treatability Tests Conducted on Groundwater from the Aerojet Propulsion Plant, Sacramento, CA"* prepared by EnviroMetal Technologies, Inc. The intent of this treatability study was to determine the rates of degradation of chlorinated volatile organic compounds and perchlorate present in groundwater using the patented EnviroMetal process (zero-valent reactive iron). The groundwater samples for the batch and column tests were collected from monitor well A41-4 located within Area 41 - Cavitt Ranch. Since its installation in August 1994, groundwater from monitor well A41-4 has had an average trichloroethylene (TCE) concentration of 228 ug/L and an average perchlorate concentration of 7,300 ug/L (for 8 sampling events).

As expected, the results of this test proved high rates of degradation of TCE with the EnviroMetal process using iron and enhanced iron. Perchlorate, however, did not show any degradation response with the EnviroMetal process using iron, enhanced iron or iron sulfide.

If you have any questions regarding the findings of this report please contact Scott Neville at (916) 355-5500 or John Vogen (EnviroMetal) at (519) 824-0432 ext. 249.

Sincerely,



Cindy L. Caulk  
Program Coordinator

**Report on the Laboratory Treatability  
Tests Conducted on Ground Water from the  
Aerojet Propulsion Systems Plant, Sacramento, CA**

**Prepared For:**

**Aerojet Environmental Operations**

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## 1.0 Introduction

Laboratory batch and column tests were conducted using the EnviroMetal Process (Gillham and O'Hannesin, 1992; 1994) to determine the rates of degradation of chlorinated volatile organic compounds (CVOCs) and perchlorate that are present in ground water at the Aerojet facility.

A batch test using two reactive materials was initially conducted to determine if CVOCs would degrade in site water containing elevated levels of perchlorate. An additional batch test was undertaken with pyrite and high levels of perchlorate. Column tests were subsequently undertaken to determine if the perchlorate would degrade under conditions of flow through two different types of reactive materials.

## 2.0 Materials

Water was collected by Environmental Operations staff of Aerojet, from Area 41 (Cavitt Ranch, the site) and sent to the Institute for Groundwater Research, University of Waterloo, Waterloo, Ontario, Canada. Water was collected from the field monitoring well, identification number A 41-4, which was considered by Aerojet staff to be representative of site conditions and suitable for use in the treatability tests.

The granular iron used in these tests was obtained from Connelly-GPM, Inc., Chicago, Illinois (-8 to +40 mesh, US Standard Sieve Mesh #). The enhanced iron was the same Connelly iron, but plated with about 0.25% nickel. The grain size ranged from 0.25 to 1.0 mm. The pyrite ( $\text{FeS}_2$ ) was obtained from North Star Minerals, Mt. Clemens, MI. It was obtained in crystalline form (2 Kg) and was crushed and sieved at the University of Waterloo, to a similar grain size range as the iron (0.25 to 2.0 mm). The specific surface area measurements were 1.8, 1.85 and 0.024  $\text{m}^2/\text{g}$  for the iron, enhanced iron and pyrite, respectively, determined by the BET method (Brunauer et. al., 1938).

### 3.0 Methodology

#### 3.1 Laboratory Batch Tests

The initial batch test was undertaken in November 1996, with A-41-4 site water which contained both trichloroethene (TCE) at 200 µg/L and perchlorate (ClO<sub>4</sub>) at 9 mg/L. The initial trichloroethene concentration was increased from 200 µg/L to approximately 7,000 µg/L, in order to have adequate time to accurately determine rates of TCE degradation from solution.

The batch test included 27 samples prepared in 40 mL glass vials. Three types of samples were prepared: blank vials, which contained only spiked site water; reactive vials containing 10 g iron and spiked site water; and enhanced iron (nickel-iron) vials containing 10 g of material and spiked site water. The mass of iron to volume of solution ratio was 1 g : 3.69 mL, while the enhanced iron vials had a mass of iron to volume of solution ratio of 1 g : 3.72 mL.

An additional batch test was undertaken with pyrite. This test was conducted with blank vials and reactive vials containing 10 g of pyrite along with site water, spiked with 100 mg/L sodium perchlorate.

For each treatability test, the site water was gravity fed into a 2 L glass bottle with a spigot at the bottom, spiked with the compound of interest and stirred on a magnetic stirrer for 30 minutes. The glass vials were filled by gravity flow, leaving no headspace, then sealed immediately with aluminium crimp caps with Teflon®-lined septa. The test vials were filled in sequence of one blank followed by a reactive vial. Sample bottles with no reactive material were also filled at the beginning, middle and end of the pouring process, to determine initial concentrations of the organic compounds, redox potential (Eh) and pH. The test vials were then placed on a rotating disc (three complete revolutions per minute), allowing for complete mixing without agitation.

At pre-determined time intervals (sampling more frequent at early times), a set of vials was removed from the rotating disc and those containing iron, enhanced iron or pyrite were centrifuged (783 g for 5 minutes) to remove suspended material. Once centrifuged, the solution samples were analysed for trichloroethene, perchlorate, Eh and pH. For each sampling time, a blank and reactive vial were sacrificed, for a maximum of nine sampling times. All tests were conducted at room temperature ( $\approx 23^{\circ}\text{C}$ ).

### 3.2 Laboratory Column Tests

Two reactive column experiments were set up: one column consisted of 100% granular iron by weight and the other was 100% enhanced granular iron by weight. The mass of iron to volume of solution ratio, along with other column parameters are shown in Table 1.

The columns were constructed of Plexiglass<sup>TM</sup> with a length of either 20 or 100 cm (0.66 or 3.3 ft) and an internal diameter of 3.8 cm (1.5 in). Several sampling ports were positioned along the column length (Figure 1). The columns also allowed for collection of samples from the influent and effluent solutions. Each sampling port consisted of a nylon Swagelok® fitting (0.16 cm) tapped into the side of the column, with a syringe needle (16G) secured by the fitting. Glass wool was placed in the needle to prevent the entry of solid material. The needles were positioned such that water samples were obtained along the central axis of the column. Each sampling port was fitted with a Luer-Lok<sup>TM</sup> fitting, such that a glass sampling syringe could be attached to the port to collect a sample. When not in operation the ports were sealed by Luer-Lok<sup>TM</sup> plugs.

Each column was carefully packed, insuring that the reactive material was homogeneously distributed. Aliquots of the reactive material were packed in lifts, taking care to avoid layering by roughening the surface of the preceding layer before adding the next layer. All measurements were determined gravimetrically and are shown in Table 1. Porosity values ranged from 0.49 to 0.58. Pore volume measurements were determined

experimentally by weight, giving values of 561 and 133 mL for the iron and enhanced iron columns, respectively. Iron to volume of solution ratios are shown in Table 1. The columns were initially flushed with carbon dioxide to avoid air entrapment during wetting. Several pore volumes of distilled water were flushed through each column before the site water was introduced. All column experiments were performed at room temperature ( $\approx 23^{\circ}\text{C}$ ).

An Ismatec<sup>TM</sup> IPN pump was used to feed the solution from a collapsible Teflon<sup>®</sup> bag to the bottom influent end of each column. The pump tubing was Viton<sup>®</sup>; all other tubing was Teflon<sup>®</sup> (0.13 in  $\times$  0.6 in). The columns were sampled periodically over time until steady state profiles were achieved. After removing stagnant water from a sampling needle, 2.0 to 5.0 mL samples were collected from the sampling ports. Samples for organic analyses and for redox potential (Eh), and pH were collected from each port. Detailed column profiling for perchlorate was also undertaken. Samples for organic and perchlorate analyses, as well as for Eh and pH measurements were also obtained from the influent solution and the effluent overflow bottles.

A flow velocity of 127 cm/day (4.2 ft/day) was used for the iron column test and a flow velocity of 83 cm/day (2.7 ft/day) was used for the enhanced iron column test.

#### 4.0 Analytical Procedures

##### 4.1 Organic Analyses

Trichloroethene (TCE) was extracted from the aqueous phase using pentane with an internal standard of 1,2-dibromoethane, at a water to pentane ratio of 2.0 to 2.0 mL. The samples were placed on a rotary shaker for 10 minutes to allow equilibration between the water and pentane phases. Using a Hewlett Packard 7673 auto sampler, a 1.0  $\mu\text{L}$  aliquot of pentane with an internal standard was automatically injected directly onto a Hewlett Packard 5890 Series II gas chromatograph. The chromatograph was equipped with a  $\text{Ni}^{63}$



electron capture detector (ECD) and DB-624 megabore capillary column (30 m x 0.538 mm ID, film thickness 3  $\mu$ m). The gas chromatograph had an initial temperature of 50°C, with a temperature time program of 15°C/minute reaching a final temperature of 150°C. The detector temperature was 300°C. The carrier gas was helium and makeup gas was 5% methane and 95% argon, with a flow rate of 30 mL/min.

Method detection limits were determined for each compound as the minimum concentration of a substance that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero. The method detection limits were determined from analysis of samples from a solution matrix containing the analytes of interest. The method detection limit for TCE was 1.7  $\mu$ g/L, which was determined using the EPA procedure for Method Detection Limit (MDL) (US EPA, 1982).

#### 4.3 Inorganic Analyses

Redox potential (Eh) was determined using a combination Ag/AgCl reference electrode with a platinum button and a Markson<sup>TM</sup> Model 90 meter. The electrode was standardized with ZoBell<sup>TM</sup>. Millivolt readings were converted to Eh, using the electrode reading and the standard potential of the Ag/AgCl electrode at a given temperature. The pH measurements were made using a combination pH/reference electrode and a Markson<sup>TM</sup> Model 90 meter, standardized with the pH buffer 7 and the appropriate buffer of either 4 or 10.

Perchlorate ion ( $\text{ClO}_4^-$ ) analysis was determined using a Cole-Parmer combination perchlorate electrode and a Markson<sup>TM</sup> Model 90 meter. Standards ranging from 1 to 1,000 mg/L were prepared from a  $\text{NaClO}_4^-$  solution. Equal amounts of sample (5 mL) and an ionic strength adjustor of 0.2 mL of 0.2 M  $(\text{NH}_4)_2\text{SO}_4$  were used to determine an electrode potential for the calibration standards, as well as the samples. A calibration

curve of  $\ln$  concentration versus electrode potential was plotted, and the perchlorate concentration was determined for each sample. A detection limit of 0.5 mg/L was obtained using this method.

## 5.0 Results and Discussion

### 5.1 Batch Results

The results of the batch tests are plotted as concentration of the organic or inorganic analyte in  $\mu\text{g/L}$  or  $\text{mg/L}$ , respectively, versus time in hours.

#### 5.1.1 Iron and Enhanced Iron

Figure 2A shows the batch results for TCE over the duration of the test (269 hr) for both the iron and enhanced iron samples. The blanks showed minor fluctuations in TCE concentration, but were relatively constant over time.

Samples from the vials containing reactive materials, both iron and enhanced iron, showed a steady decline in TCE concentration from an initial value of 7,183  $\mu\text{g/L}$  to non-detectable concentrations at the conclusion of the test (270 hr), Figure 2A. Up to a time of 48 hr, the iron showed a slightly greater decline over enhanced iron. At later times the curves converge with no significant difference between the iron and enhanced iron results.

Degradation rate constants were calculated for the organic compounds using the first-order kinetic model:

$$C = C_0 e^{-kt} \quad (1)$$

where  $C$  is the organic concentration in solution at time  $t$ ,  $C_0$  is the initial concentration (organic concentration at  $t_0$ ),  $k$  is the first order rate constant, and  $t$  is time. By rearranging and taking the natural log, equation 1 becomes:

$$\ln (C/C_0) = -kt \quad (2)$$

The time at which the initial concentration declines by one-half, ( $C/C_0 = 0.5$ ), is the half-life, which, by rearranging equation 1, is given by:

$$t_{1/2} = 0.693 / k \quad (3)$$

The decay constants,  $k$  [1/time], were computed from the slope of the first-order model, obtained by fitting equation 2 to a semi-log plot of the experimental data. Half lives for the batch test and the corresponding coefficients of variation ( $r^2$ ) are listed in Table 2. The  $r^2$  values indicate the degree to which the first-order model represents the experimental data.

The first-order decay model provided good fits to the TCE data for both materials, with  $r^2$  values of  $>0.84$ . The half life for granular iron was 24 hr and a half life of 27 hr was obtained for the enhanced iron. These results are consistent with batch tests performed using groundwater from other sites.

The perchlorate ( $\text{ClO}_4^-$ ) concentration (mg/L) over time is shown in Figure 2B for both the iron and enhanced iron. The blank concentration declined from an initial concentration of 9 mg/L to 3-6 mg/L over the time interval of 48-269 hr. The reason for this decline is unclear. The reactive vials showed a decline in concentration from 9 mg/L to about 4 mg/L for both materials. However, the testing was inconclusive as to whether the decline was a result of degradation or sorption onto the iron surface.

The redox potential (Eh) showed slightly reducing conditions, declining from +300 to about -100 mV for both types of reactive materials, while the blanks maintained the initial values of +300 mV (Figure 3A). The pH remained relatively constant in the blank vials at 7.3, while a slight decline in pH was observed to values between 6.5 and 7.0 for both the iron and enhanced iron (Figure 3B).

### 5.1.2 Pyrite

Figure 4 shows the results for the batch test conducted with pyrite at an initial perchlorate concentration of 100 mg/L. There was no observed decline in perchlorate concentration in either the reactive pyrite vials nor the blanks over the duration of the 190 hr test.

The Eh was maintained in the blank vials (+400 mV), however an increase was observed to +500 mV in the pyrite vials (Figure 5A). The initial pH value of 8.0 was maintained in the blank vials, but the pyrite vials showed a decrease in pH to 3.0.

## 5.2 Column Results

The water that was used in the column testing was simulated groundwater consisting of 40 mg/L calcium carbonate spiked with perchlorate at a concentration of about 100 mg/L. Concentration profiles along the columns were measured over numerous pore volumes. The results are plotted as concentration (mg/L) versus distance along the column (cm) over various pore volumes.

### 5.2.1 Iron

Concentration profiles for perchlorate along the length of the iron column are shown in Figure 6. At a flow velocity of 127 cm/day (4.2 ft/day), a total of 28 pore volumes of water had passed through the column. The profiles are shown for various sampling times. In this case, one pore volume corresponds to a residence time of 19 hr. Throughout the

testing, it appeared that the perchlorate concentration remained relatively constant. With an initial concentration of 80 mg/L, the effluent concentration was very similar to the influent with concentrations ranging from 75 to 86 over the testing period. The redox potential showed reducing conditions along the column profile with values of -400 mV, while the pH increased from a value of 7.5 to 10 along the length of the column (Figure 7A&B).

### 5.2.2 Enhanced Iron

Figure 8 shows the results of the enhanced iron column. This column had a flow velocity of 83 cm/day (2.7 ft/day), with a corresponding residence time of 5.8 hr. Due to the nature of the enhanced iron column, and a column length of 20 cm, 130 pore volumes of water passed through the column. Similar trends were observed as in the iron column, with little to no decline in perchlorate concentration over the duration of the test. Reducing conditions were observed -300 mV, while pH values ranged from 7.6 to 9.0 over the length of the column (Figure 9A&B).

## 6.0 Conclusion

In the batch tests, TCE showed high rates of degradation using the EnviroMetal Process for both the iron and enhanced iron. However, the enhanced iron did not appear to have any rate advantage over regular untreated iron. It appeared that the perchlorate concentration was unaffected by either iron, enhanced iron or pyrite in either static batch tests or dynamic column tests.

## 7.0 References

Brunauer, S., Emmett, P.H., and Teller, E., 1938. Adsorption of gases in multimolecular layers. J. American Chemical Society, Vol 60, pp. 309-319.

Gillham, R.W. and O'Hannesin, S.F., 1994. Enhanced degradation of halogenated aliphatics by zero-valent iron. Ground Water, Vol. 32, No. 6, pp. 958-967.

Gillham, R.W. and O'Hannesin, S.F., 1992. Metal-catalysed abiotic degradation of halogenated organic compounds. IAH Conference "Modern trends in hydrogeology", Hamilton, Ontario, May 10-13, pp. 94-103.

United States Environmental Protection Agency, 1982. Methods for organic chemical analysis of municipal and industrial wastewater; EPA-600/4-82-057, J.E. Longbottom and J.J. Lichtenberg (eds.); Cincinnati, Ohio; Appendix A.

**Table 1: Column properties**

Column Composition	100% Iron	100% Enhanced Iron
Flow Velocity (cm/day)	127	83
(ft/day)	4.2	2.7
Residence Time (hr)	19.0	5.8
Pore Volume (mL)	561	133
Porosity	0.49	0.58
Iron to Volume of Solution Ratio ( g:mL )	6.05 : 1	4.72 : 1

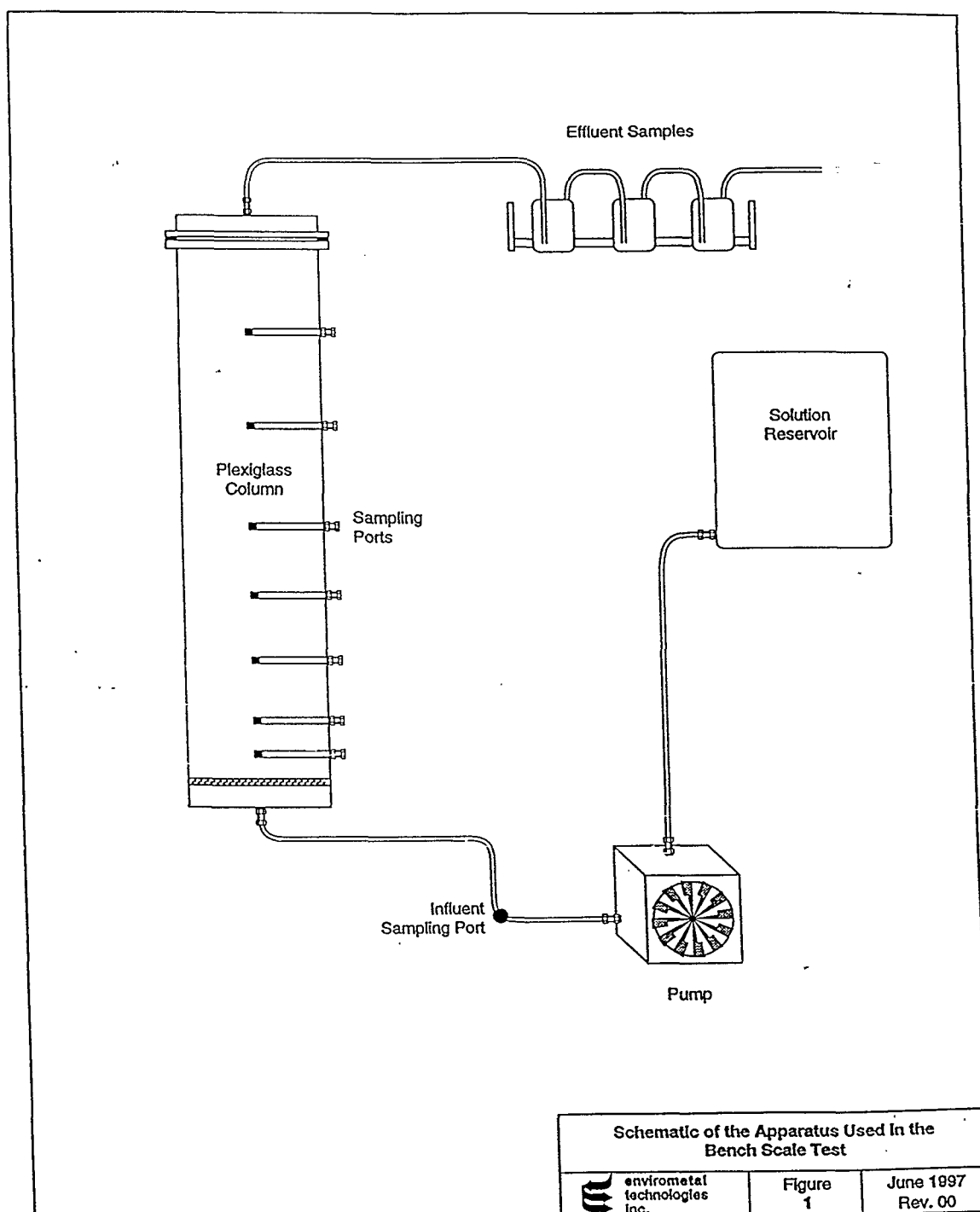
**Table 2:** Half lives ( $t_{1/2}$ ) generated from the organic batch test results using spiked TCE in Aerojet site water. The coefficients of variation [ $r^2$ ] were determined by fitting the first-order decay equation to the experimental data.

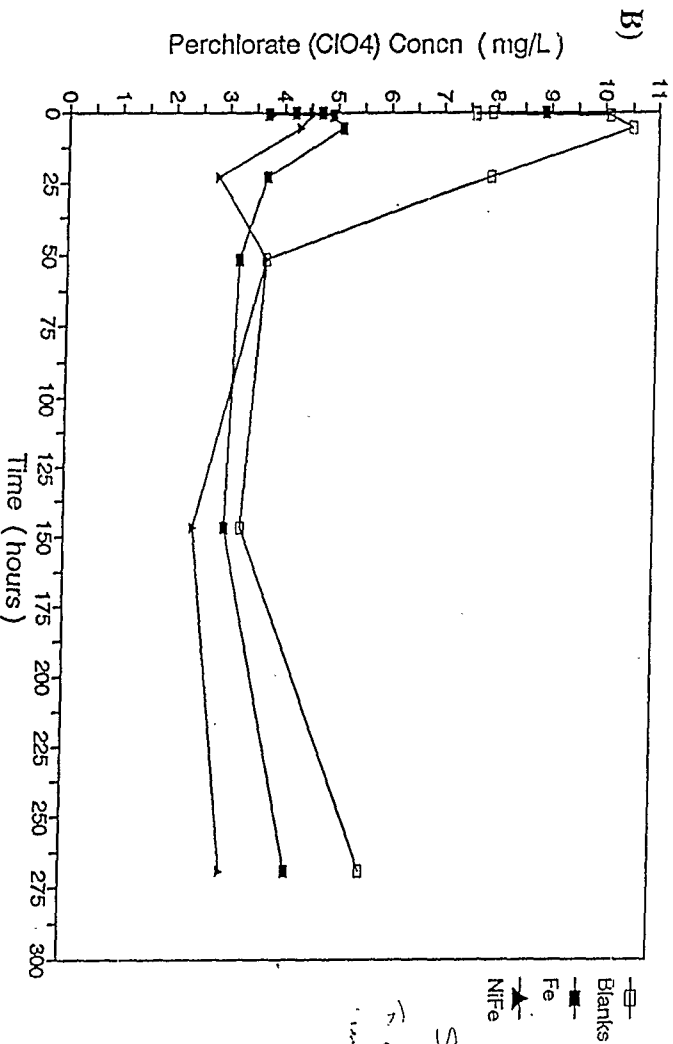
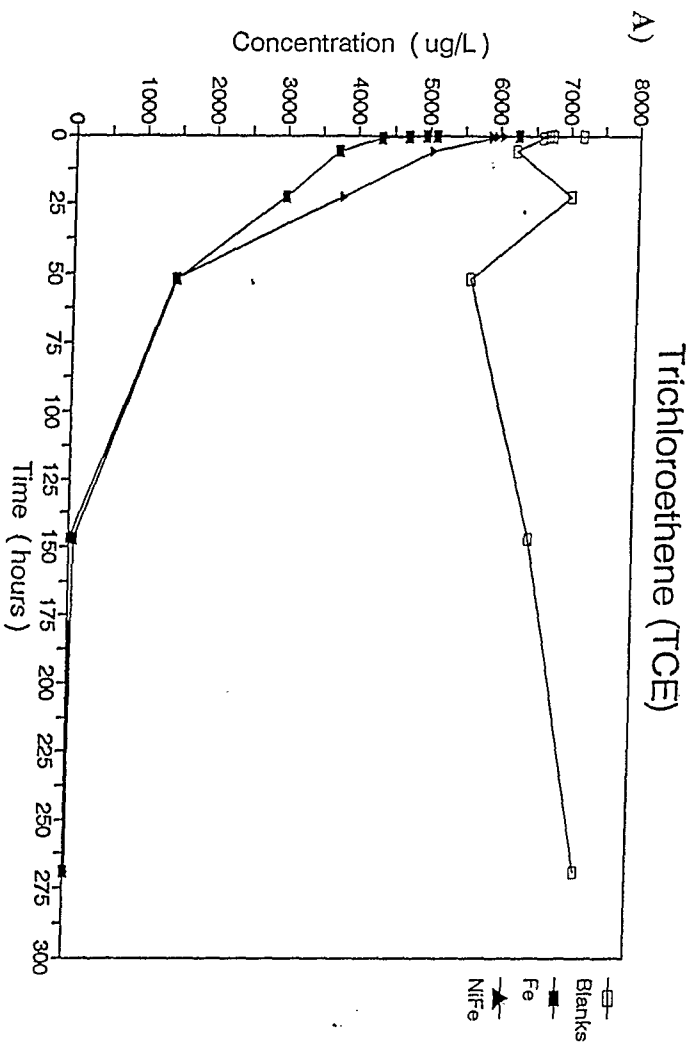
Compound	Initial Concn ( $\mu\text{g/L}$ )	Iron $t_{1/2}$ , [ $r^2$ ] (hr)	Enhanced Iron $t_{1/2}$ , [ $r^2$ ] (hr)
Trichloroethene	7183	23.9 [0.989]	26.9 [0.837]

$t_{1/2}$  = half life (hours)

$r^2$  = coefficient of variation







Sampled from AT  
 location in the  
 unknown

**Figure 2:** Batch tests results with iron and enhanced iron. Concentration versus time. A) TCE B) Perchlorate

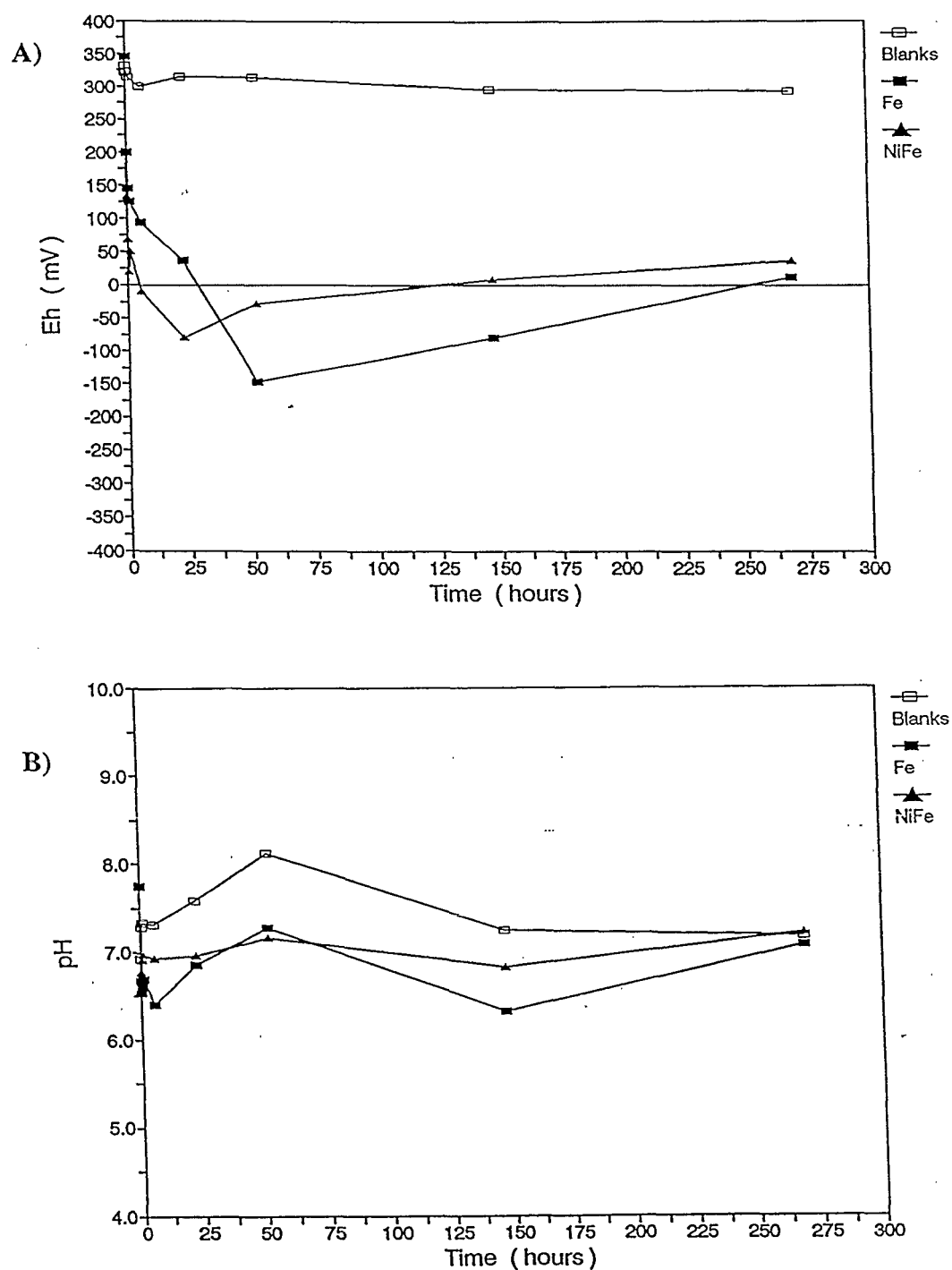
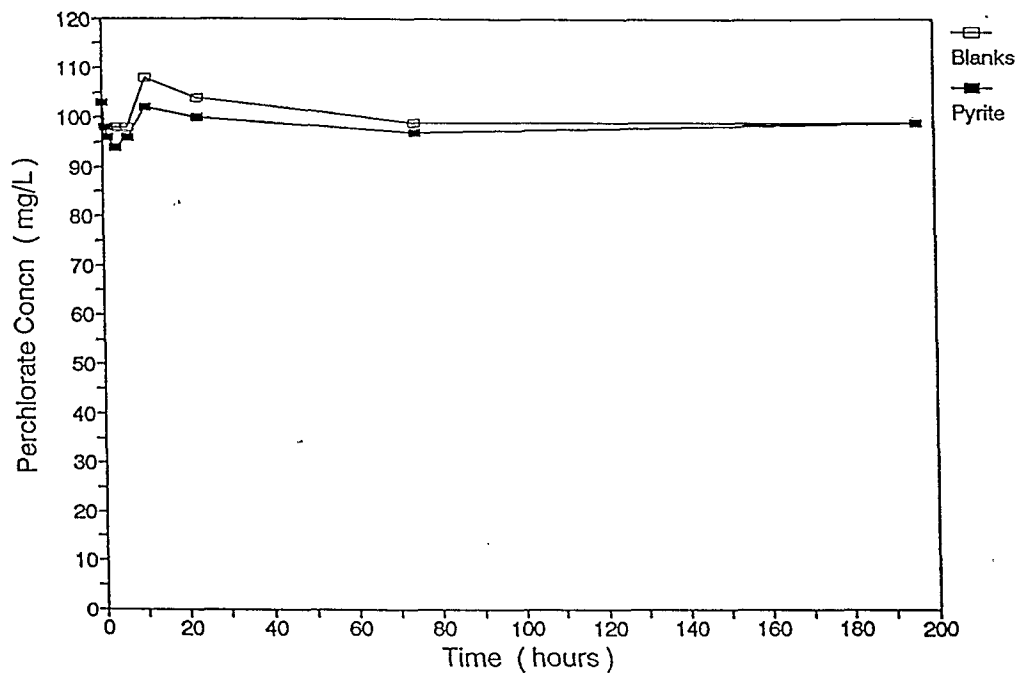


Figure 3: Batch tests results with iron and enhanced iron. A) Eh versus time  
B) pH versus time



**Figure 4:** Batch test results with pyrite and spiked perchlorate site water. *10 ppb (lab generated sample)*  
Concentration versus time.

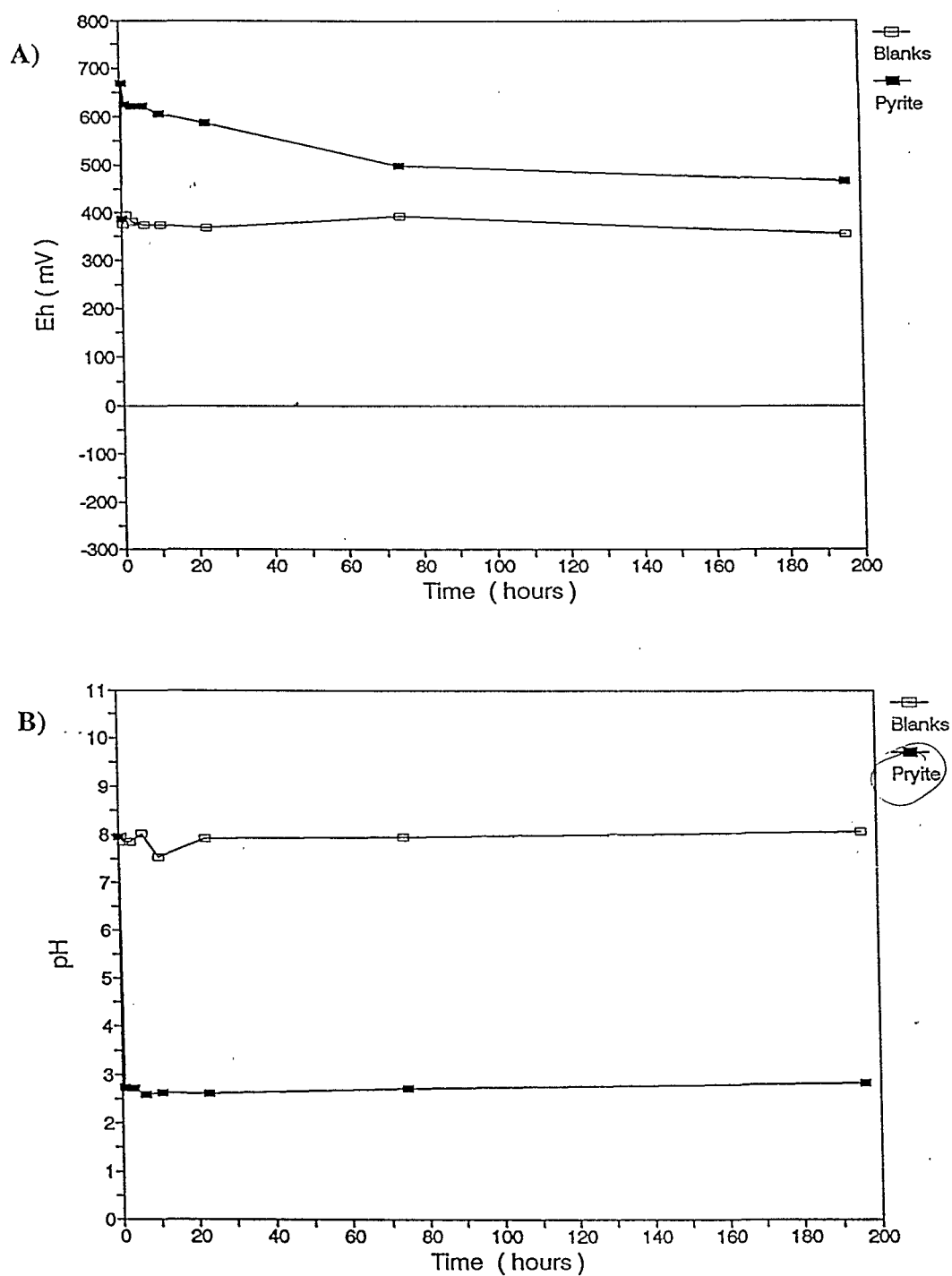
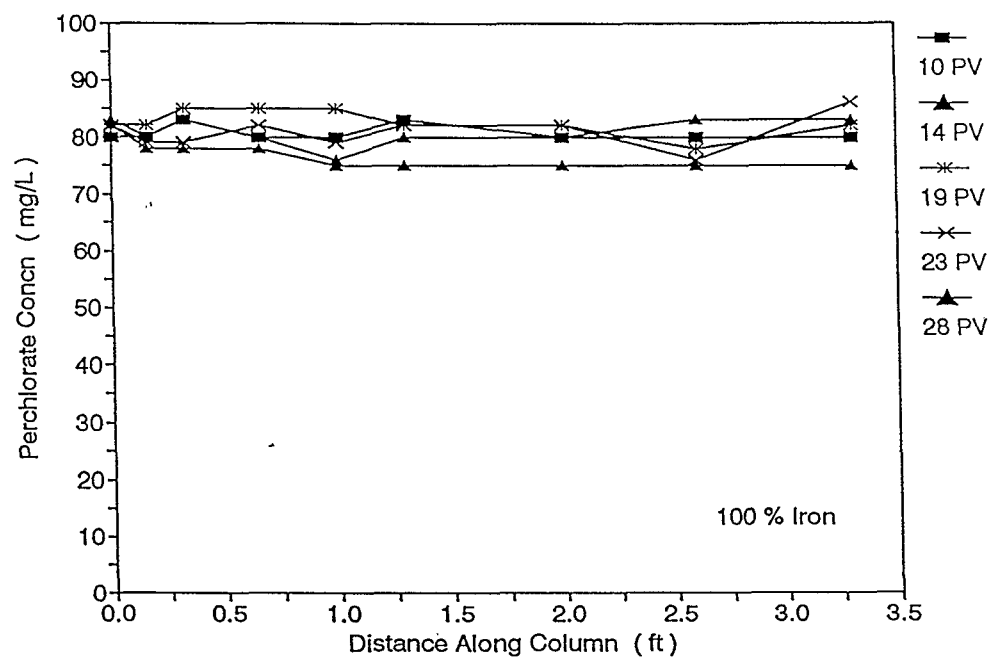
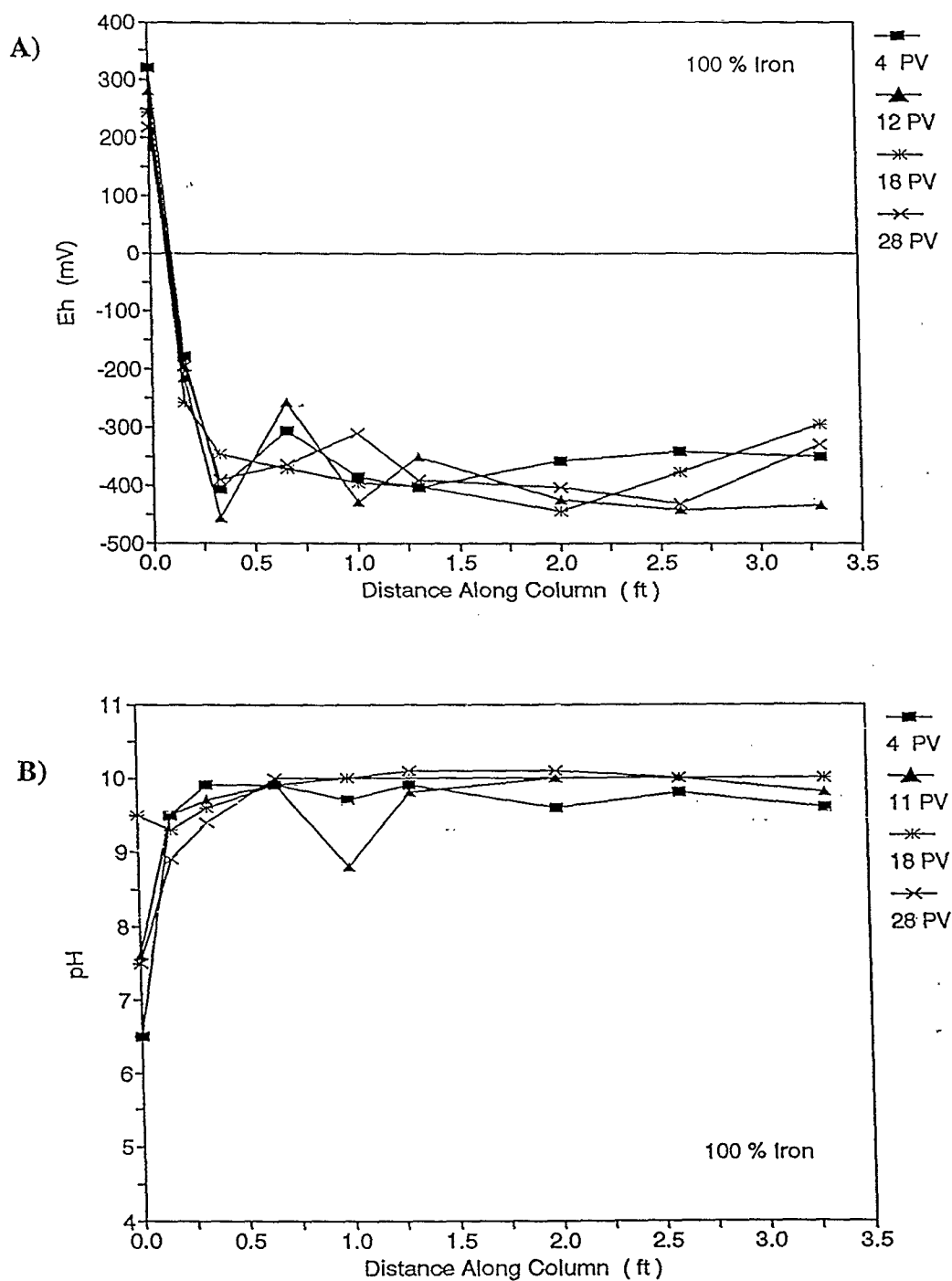


Figure 5:

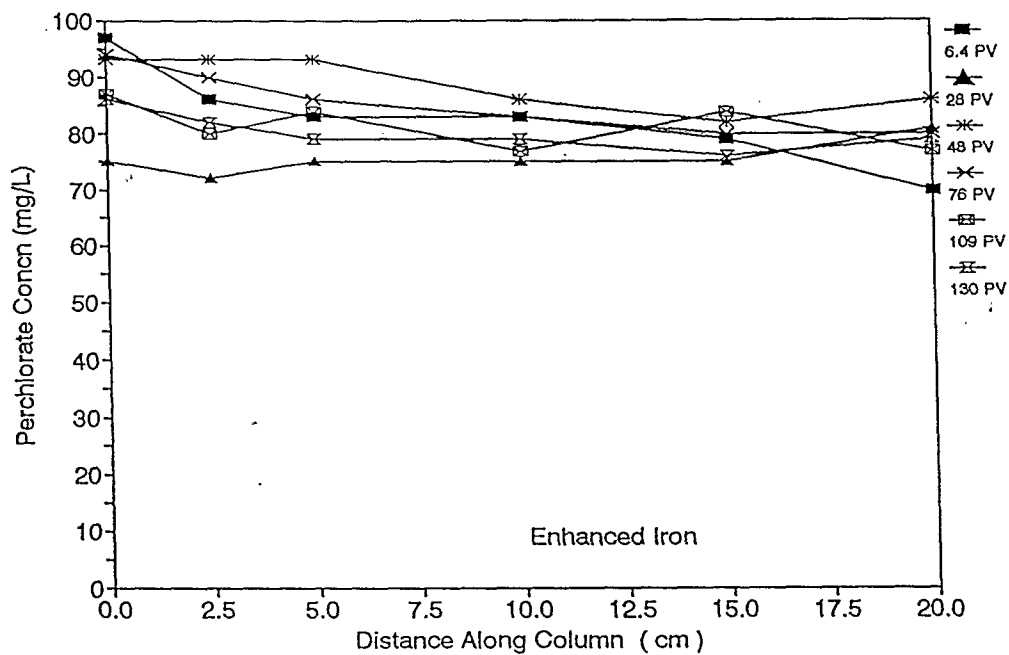
Lab generated sample  
Batch test results with pyrite and perchlorate. Concentration versus time.  
A) Eh versus time B) pH versus time



**Figure 6:** Iron column test results and perchlorate. Concentration versus distance along the column over various pore volumes.

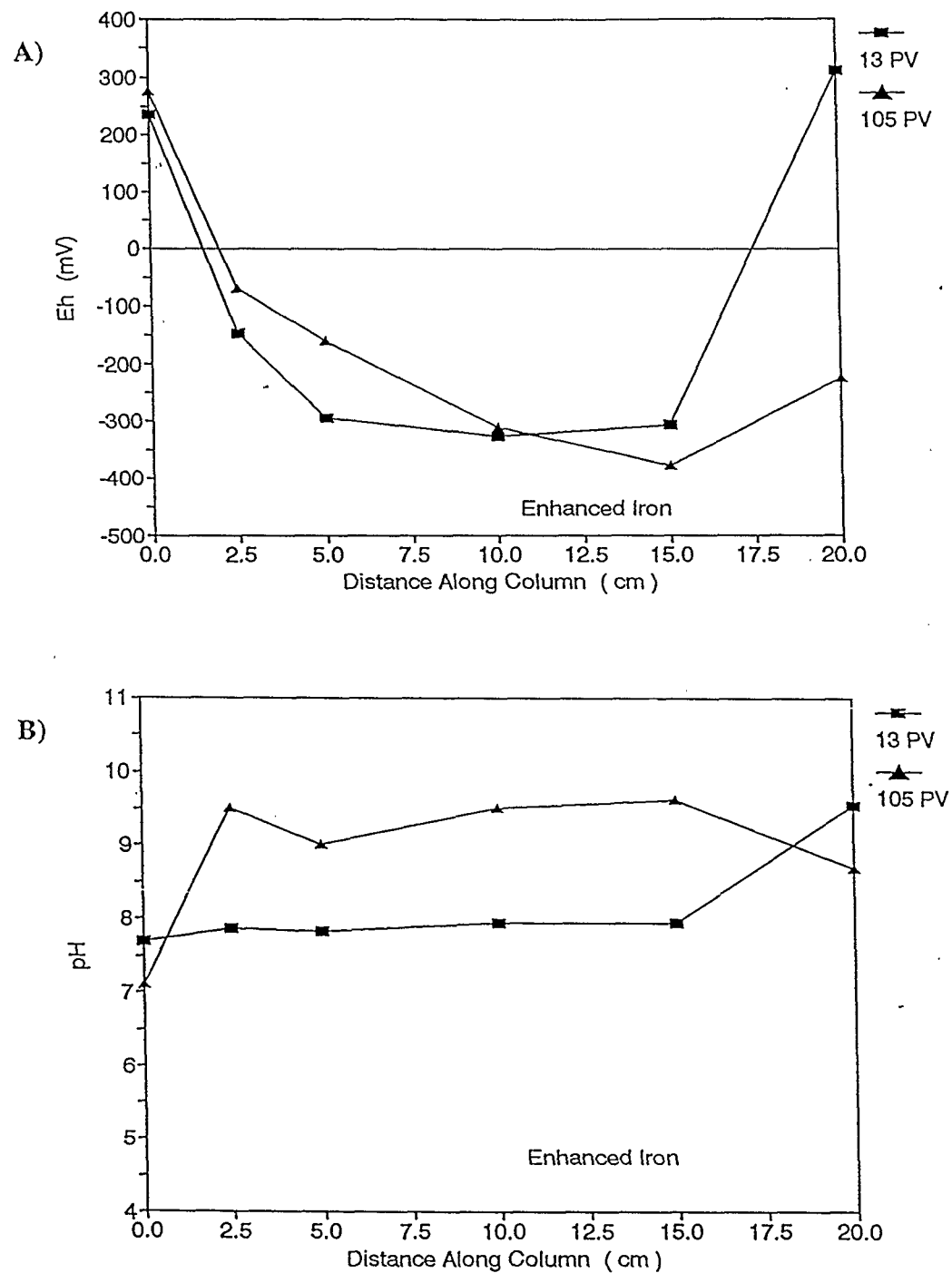


**Figure 7:** Iron column test results and perchlorate. A) Eh versus distance over various pore volumes B) pH versus distance over various pore volumes.



**Figure 8:** Enhanced iron column test results and perchlorate. Concentration versus distance along the column over various pore volumes.





**Figure 9:** Enhanced iron column test results and perchlorate. A) Eh versus distance over various pore volumes B) pH versus distance over various pore volumes.